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(54) FINE ZINC OXIDE PARTICLES, PROCESS FOR PRODUCING THE SAME, AND USE THEREOF

(57) A process for producing zinc oxide fine particles comprising heating a mixture comprising a zinc source, a carboxyl-containing compound, and an alcohol; a process for producing zinc oxide-polymer composite particles, which comprises heating a mixture comprising a zinc source, a carboxyl-containing compound, a polymer, and an alcohol at a temperature of 100°C or higher; a process for producing inorganic compound particles having on their surface a cluster of thin plate like zinc oxide crystals with their tip projecting outward, which comprises heating a mixture comprising a zinc source, a carboxyl-containing compound, lactic acid or a compound thereof, and an alcohol at a temperature of 100°C or higher; a process for producing zinc oxide-based particles comprising heating a mixture comprising a zinc source, a carboxyl-containing compound, at least one element additive selected from the group consisting of the group IIIB metal elements and the group IVB metal elements, and an alcohol at a temperature of 100°C or higher; zinc oxide-based fine particles obtained by these processes; and uses of the zinc oxide-based fine particles.

Fig. 1

1 μm

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Description

Technical Field

This invention relates to a process for producing zinc oxide-based fine particles which are useful as a raw material or an additive for rubber vulcanization accelerators, various coatings, printing inks, colors, glass, catalysts, medicines, pigments, ferrite, etc. and can also be made use of in electrophotographic photoreceptors, printing materials, platemaking materials, UV screens, UV absorbing materials, gas sensors, etc. It also relates to a process for producing zinc oxide-based fine particles which are useful as such an additive that has high light-transmitting properties in the visible region and high UV absorbing properties, i.e., a so-called transparent UV absorber in coating materials, varnishes, resins, paper, cosmetics, and the like.

The present invention relates to zinc oxide-based fine particles having high transparency in the visible region, excellent UV absorbing properties, and heat ray screening properties as well as the above-mentioned functions and uses, which are useful as a so-called transparent UV and heat ray screening agent, an electrically conducting agent or an antistatic agent that in coatings (e.g., coating agent, ink, etc.), resins, paper, cosmetics, etc.; a process for producing the same; and products containing the same, i.e., coatings, coated articles, resin compositions, resin molded articles, cosmetics, and paper.

The present invention relates to zinc oxide-based fine particles which have a unique higher-order structure in which the constituent primary particles (zinc oxide crystals) have a controlled size and therefore exhibit high light transmitting properties combined with excellent scattering properties in the visible region, that is, excellent diffuse transmission properties in addition to the above-described functions and uses. The fine particles are therefore useful as a light diffusing agent. The invention also relates to a process for producing such zinc oxide-based particles and products containing the same, such as coatings (e.g., coating agent, ink, etc.), coated articles, resin compositions, resin molded articles, cosmetics, and paper, typified by a medium for diffuse transmission, such as a diffuser film for back-lighting liquid crystal displays.

The present invention relates to zinc oxide-based fine particles which not only have the above-described functions and uses but have controlled crystal morphology and a unique agglomerated state (higher-order structure) and are therefore also excellent in antimicrobial properties and deodorizing properties; a process for producing the same; and products containing the same, such as coatings (e.g., coating agent, ink, etc.), coated articles, resin compositions, resin molded articles, cosmetics, and paper.

Background Art

Zinc oxide fine particles, what we call zinc white, have been conventionally produced by (1) a method consisting of gas phase oxidation of zinc vapor (called a France process or a American process) or (2) a method comprising reacting a zinc salt and an alkali metal carbonate in an aqueous solution to obtain zinc carbonate powder and, after washing with water and drying, pyrolyzing the powder in air. Zinc oxide obtained by the method (1) appears to have a particle size of submicron order but undergoes strong secondary agglomeration during the production process. Dispersing the particles in coating compositions or resin compositions requires much mechanical labor and yet results in a failure of obtaining a homogeneous dispersion. Compared with the method (1), the method (2) provides such finer particles as have a primary particle size of 0.1 μm or smaller, but the effects expected from the fineness are not manifested sufficiently on account of the strong agglomerating force among primary particles. Under the present situation, it is still less achievable with these methods to obtain zinc oxide fine particles with strictly controlled morphology, such as particle size, shape and surface condition of the primary particles, and the state of dispersion or agglomeration, in agreement with the end use.

In recent years, development of zinc oxide-based fine particles practically having a particle size of not greater than 0.1 μm has been demanded for use as a weatherable and heat-resistant material which is highly transparent in the visible region and also capable of absorbing ultraviolet light, i.e., a so-called transparent UV absorber. Processes hitherto proposed for producing such fine particles include (3) a method comprising gas phase oxidation of zinc vapor and (4) a wet process, such as a process comprising hydrolysis of a zinc salt in an alkali aqueous solution (see JP-A-4-164813 and JP-A-4-357114, the term "JP-A" as used herein means an "unexamined published Japanese patent application") and a process in which a mixed solution of an acidic salt of zinc and ammonium acetate and hydrogen sulfide are subjected to autoclaving to form zinc sulfide, which is then subjected to oxidation (see JP-A-2-311314). The fine particles as obtained by the method (3) are powder having undergone firm secondary agglomeration as stated above and, when added to plastic moldings, such as fiber, a plate or a film, or coatings for the purpose of imparting UV absorptivity or improving weatherability, fail to provide products having satisfactory transparency. Further, when the fine particles are dispersed in an appropriate solvent and, if necessary, mixed with a binder resin to prepare a coating agent, and the coating agent is applied to a transparent substrate, such as glass or a plastic film, for the purpose of imparting UV absorptivity, the resulting coating film has poor transparency and homogeneity. On the other hand, the wet processes

(4) involve complicated steps and unavoidably incur high cost. Thus, a process for producing zinc oxide-based fine particles which manifest the functions and characteristics of fine particles to the full extent and still have general-purpose properties is unknown.

Since zinc oxide fine particles have excellent UV screening power (in absorbing or scattering), they are used in coating films or resin molded articles endowed with UV screening power. However, zinc oxide fine particles have low dispersibility due to their liability to agglomeration.

Light-diffusing compositions comprising transparent inorganic fine particles, e.g., calcium carbonate, silica or barium sulfate, as dispersed in a binder component capable of dispersing such fine particles (e.g., methacrylic resins) are known. The light-diffusing compositions are used as a coating composition to be applied to a transparent substrate to form a light-diffusing layer or as a molding material to be molded into a molded article having light-diffusing properties, to provide a diffuser. The diffusing properties of these diffusers are based on light scattering at the interface between the inorganic transparent fine particles and the binder component due to the difference in refractive index therebetween.

However, the inorganic transparent particles of calcium carbonate, silica, barium sulfate, and the like do not have a UV screening function. Further, these diffusers essentially have poor mechanical characteristics on account of low affinity between the inorganic transparent particles and the binder component. Furthermore, since the diffusers should contain a large quantity of the inorganic transparent particles for achieving high diffusing properties, they have a reduced percent transmission and further reduced mechanical characteristics.

There has recently been an increasing demand for antistatic treatment on glass products or plastic products (films and fibers) for use as window panes of a clean room, CRT screens, flooring, wall covering, clothing, and the like for the purpose of preventing adhesion of dust.

An insulator, such as resin, can be made electrically conductive by, for example, dispersing a conducting agent in resin or applying a coating composition having dispersed therein a conducting agent on a substrate to form an electrically conductive layer. Known conducting agents include fine particles of metals, e.g., nickel (Ni), copper (Cu) or aluminum (Al); fine particles of metal oxides, such as those obtained by reducing metal oxides represented by titanium black, and electrically conducting white metal oxides activated with different elements (e.g., tin oxide-based particles, indium oxide-based particles, and zinc oxide-based particles); carbonaceous fine particles of carbon black, graphite, etc.; and organic conducting agents represented by nonionic, anionic, cationic or amphoteric surface active agents.

Of these conducting agents, organic ones, whose conductivity-imparting action is based on ionic conduction and therefore dependent on humidity, unsuccessfully work at a low humidity. Besides, those having a low molecular weight bleed out with time and undergo deterioration in performance.

To the contrary, metallic, metal oxide type, or carbonaceous conducting agents, whose action is based on electron conduction, are substantially independent on humidity. Although superior to organic ones in this point, the metal oxide conducting agents obtained by reduction of titanium black, etc. and the carbonaceous conducting agents assume a black or nearly black color, and the metallic conducting agents reflect visible light strongly. Therefore, it is extremely difficult to retain the transparency of the substrate or matrix, and the application of these conducting agents is so limited.

On the other hand, it is known that a coating film formed of ink or a coating composition having dispersed therein such white conducting particles as antimony-doped tin oxide and tin-doped indium oxide or a film formed of a resin composition having dispersed therein these particles successfully impart conductivity for producing antistatic effect without impairing the hue of the substrate or the matrix. A film formed of these oxides by gas phase film formation, such as sputtering, has high electrical conductivity and has been used as a transparent electrode of flat displays, such as liquid crystal displays and electroluminescence displays, an electrode for touch panels of word processors, electronic game equipment, etc., and an antistatic film. However, because the raw materials of tin oxide- or indium oxide-based particles are very expensive, and gas phase film formation requires expensive equipment, this technique does not seem applicable generally.

In recent times, a material has been demanded, which can be applied to or incorporated into glass products, such as window panes, or resin products, such as polyester or (meth)acrylic films or sheets, without impairing the transparency or hue of the substrate or matrix and effectively shield these products from ultraviolet rays, inclusive of UV-B (280 to 320 nm) and UV-A (320 to 400 nm), and heat rays.

Conventional materials known for their UV screening effect include organic UV absorbers, such as benzotriazole compounds and benzophenone compounds, and inorganic UV absorbers, such as titanium oxide, zinc oxide, and cerium oxide. However, none of them has a heat ray screening effect.

Known heat ray screens include organic dyes having absorptivity in the infrared region, such as anthraquinone type, polymethine type, cyanine type, aluminum type or diimonium type dyes, and the aforementioned tin oxide- or indium oxide-based conducting particles, but none of them screens out ultraviolet rays effectively.

It is known that fine particles of mica coated with a titanium oxide thin film absorb ultraviolet light owing to the titanium oxide coat and, having a multi-layer structure, scatter electromagnetic waves in the heat ray region to some extent. However, the particles have insufficient visible light transmitting properties and are not deemed to fit the above-described needs.

Considering a combined use of a UV screen and a heat ray screen, there are disadvantages such that the organic dye (heat ray screen) shows absorptions in the visible light and unavoidably causes coloring; the heat ray absorption range of the organic dye is narrow; and the tin oxide- or indium oxide-based particles are expensive and economically disadvantageous as stated above.

Zinc oxide effectively absorbs both A and B waves of ultraviolet light and shows no selective absorption in the visible region. Therefore, a thin film having highly dispersed therein ultrafine particles of zinc oxide or a homogeneous zinc oxide thin film obtained by gas phase film formation serves as a transparent UV absorbing film. Doping of zinc oxide with a trivalent or tetravalent metal element gives zinc oxide electrical conductivity and, in some cases, heat ray screening properties.

However, as stated above, a process for producing zinc oxide fine particles which can manifest the functions and characteristics of fine particles to the full extent and still have general-purpose properties is unknown. Besides, all the zinc oxide fine particles so far obtained by conventional processes have UV absorbing properties but cannot screen out (near) infrared rays.

On the other hand, it is known that a zinc oxide film comprising zinc oxide doped with aluminum (Al) which is obtained by gas phase film formation exhibits high electrical conductivity and heat ray screening power (see Minami Uchitsugu, Ohyo Butsuri (Applied Physics), Vol. 61, No. 12 (1992)). It has been suggested that a solid solution of silicon (Si), germanium (Ge), zirconium (Zr), etc. in zinc oxide (JP-B-5-6766, the term "JP-B" as used herein means an "examined published Japanese patent application"), a solid solution of the group IIIB element, e.g., boron (B), scandium (Sc), yttrium (Y), indium (In), thallium (Tl), etc., in zinc oxide (JP-B-3-72011) or a solid solution of aluminum (Al) in zinc oxide (JP-B-4-929) can provide a transparent zinc oxide film excellent in conductivity and infrared reflecting properties. However, any of the techniques disclosed consists of gas phase film formation and cannot be a general-purpose process.

It is also known that an electrically conductive zinc oxide film can be obtained by a method for forming a zinc oxide thin film making use of pyrolysis of a zinc salt, in which the film is finally subjected to high temperature in a reducing atmosphere, or a dopant is previously added to a zinc salt solution and a resulting film is finally subjected to high temperature, as disclosed in JP-A-1-301515. This method still fails to provide heat ray screening properties.

Additional methods which are generally known for making zinc oxide powder electrically conductive include a method comprising calcining zinc oxide powder at a high temperature in a reducing atmosphere and a method comprising calcining zinc oxide powder mixed with a dopant, e.g., aluminum oxide, at a high temperature in a reducing atmosphere. The degree of conductivity attained by the former method is limited. In either method, because the particles are exposed to high temperature, fine particles, especially ultrafine particles of 0.1 μm or smaller cannot be obtained.

A transparent conducting film-forming composition containing conductive zinc oxide fine powder prepared by a specific process is known (JP-A-1-153769), in which the conductive zinc oxide fine powder is aluminum-activated powder having a specific surface area diameter of not greater than 0.1 μm and a volume resistivity of not higher than 10^4 Ωcm under a specific pressure condition. However, since the preparation of the zinc oxide powder involves calcination at a high temperature, the powder, even having a specific surface area diameter of not greater than 0.1 μm, becomes larger as dispersed in the composition. It is assumed that the film obtained by application of the coating composition would have limited transparency. Heat ray screening properties of the film according to this technique are unknown.

Fine and thin particles of inorganic compounds having a tabular form, a flaky form and the like include titanium oxide fine particles (JP-A-58-88121), titanium oxide-coated mica (JP-B-31-9355, JP-B-33-294, and JP-A-2-173060), and zinc oxide fine flakes (JP-B-55-25133 and JP-A-6-80421).

These inorganic compound fine particles are added to resin compositions forming film, fiber or plates; coating compositions to be applied to film, fiber, resin plates, glass, paper, etc.; paper; cosmetics; and the like for the purpose of adding value to these products.

Inorganic compound fine particles which are added to resin compositions forming film, fiber or plates; coating compositions to be applied to film, fiber, resin plates, glass, paper, etc.; paper; cosmetics; and the like for the purpose of improving appearance, energy saving, and improving comfort of household goods in conformity with an advanced style of life are required to have:

(1) an attractive appearance brought about by designing to the effect that a tone changes with a change in viewing angle or angle of light incidence and also by transparency; and
(2) a function of efficiently cutting heat rays, particularly near infrared rays, in seeking energy saving and comfort.

For protection of the body, particularly hair, eyes and the skin and for prevention of deterioration of resin products, the inorganic compound fine particles possessing the above characteristics (1) and (2) are additionally required to have (3) a function of efficiently cutting ultraviolet rays which are contained in sunlight or electromagnetic waves emitted from fluorescent tubes and cause harm to the body and deterioration in resin products. UV screens comprising inorganic compound fine particles are superior to organic UV absorbers in terms of toxicity, heat resistance, and stability with time. From this viewpoint, TiO_2 or ZnO has been made into ultrafine particles or thin particles for use for transparency improvement.

Ultrafine or thin titanium oxide particles do not possess the above-described effects of design, though having a UV cutting effect and higher visible light transmitting properties than titanium white that is a white pigment.

Although titanium oxide-coated mica is capable of preventing transmission of heat rays and ultraviolet rays, they have a pearly luster, lacking transparency, and is therefore inferior in terms of the above-mentioned attractiveness of appearance.

Ultrafine or thin plate like zinc oxide particles have transparency to visible light and, as compared with titanium oxide fine particles, cut ultraviolet rays over a longer wavelength side, and retain the UV cutting effect over an extended time period. However, zinc oxide fine particles do not possess the above-described effect of design and transmit heat rays.

An object of the present invention is to provide a highly productive process for producing zinc oxide fine particles with their size, shape and surface conditions controlled and also with the degree of dispersion and agglomeration controlled, which comprises heating a mixture of zinc or a compound thereof, a carboxyl-containing compound, and an alcohol.

Another object of the invention is to provide an industrial process for producing zinc oxide fine particles which can manifest the functions and characteristics of fine particles having excellent transparency to the full extent in practical use.

Still another object of the invention is to provide zinc oxide-polymer composite particles which exhibit UV screening power, controlled visible light transmitting properties combined with controlled light diffusing properties, and excellent dispersibility.

Yet another object of the invention is to provide a process for producing such zinc oxide-polymer composite particles with satisfactory productivity.

A further object of the invention is to provide inorganic compound particles which show abnormal light transmitting properties ascribed to their unique geometrical characteristics not heretofore attained.

A still further object of the invention is to provide a process for producing such inorganic compound particles with satisfactory productivity.

A yet further object of the invention is to provide zinc oxide-based particles which comprise zinc oxide having excellent UV screening properties as a base to which heat ray screening properties and electrical conductivity are imparted, and which are easily made transparent.

A yet another object of the invention is to provide a process for producing such zinc oxide-based particles with high productivity.

A yet another object of the invention is to provide coating compositions, coated articles, resin compositions, resin molded articles, paper, and cosmetics which contain the above-described zinc oxide fine particles, zinc oxide-polymer composite particles, inorganic compound particles or zinc oxide-based particles so that the characteristics possesses by these particles may be taken advantage of.

Disclosure of the Invention

The inventors of the present invention have conducted extensive investigations in order to accomplish the above objects and, as a result, reached the invention.

The invention embraces the following embodiments.

(1) A process for producing zinc oxide fine particles comprising heating a mixture comprising a zinc source, a carboxyl-containing compound, and an alcohol.

(2) A process for producing zinc oxide fine particles as described in (1), which comprises a first mixing step of preparing a first mixture comprising a zinc source and a carboxyl-containing compound and a second mixing step of mixing the first mixture with a heated alcohol-containing solution.

(3) A process for producing inorganic compound particles as described in (2), wherein the second mixing step is a step of adding the first mixture to an alcohol-containing solvent maintained at 100°C or above and mixing them.

(4) A process for producing zinc oxide fine particles as described in any of (1) to (3), wherein the process comprises a first mixing step of preparing a first mixture comprising a zinc source and a carboxyl-containing compound, a second mixing step of mixing the first mixture maintained at 60°C or above with an alcohol-containing solution maintained at 100°C or above to obtain a second mixture, and a step of heating the second mixture.

(5) A process for producing zinc oxide fine particles as described in any of (1) to (4), wherein the resulting zinc oxide fine particles have an average primary particle size ranging from 0.005 to 10 μm.

(6) A process for producing zinc oxide fine particles as described in any of (1) to (5), wherein the zinc source is selected from the group consisting of zinc oxide, zinc hydroxide, and zinc acetate.

(7) A process for producing zinc oxide fine particles as described in any of (1) to (6), wherein the carboxyl-containing compound comprises a saturated fatty acid having a boiling point of 200°C or lower at atmospheric pressure.

(8) A process for producing zinc oxide fine particles as described in any of (4) to (7), wherein the second mixing